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Wave-length Measurements in Spectra from 5600A to 9600A.

DISSERTATION

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Wave-length Measurements in Spectra
from

5600 A. to 9600 A.

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I. Introduction.

During the past thirty years the spectra of the chemical elements have been quite thoroughly investigated in the wave-length region to which ordinary photographic plates are most sensitive, that is, from 2000 A to 6000 A. (A = Angstrom = 0.0000001 mm). This was made possible by Professor Rowland's invention of the concave grating and the establishment of his system of standard wave-lengths. Since 1904 a new system of wave-length standards - the International system - has been established and the wave-lengths from 2000 A to 6000 A of many spectra have been re-measured in International Angstroms.

The long waves have never been so extensively or carefully investigated because of the great difficulty in photographing them. Measurements of the wave-lengths of some of the strong lines in the red and adjacent infra-red regions of the spectrum have been made by using radiometers or phosphoro-photography to detect the waves. These methods are also difficult and yield results which are not in very good agreement. It is generally conceded that nothing can compete with direct photography for the accurate determination of the structure and wave-lengths of spectral lines.

The photographic work on long wave-lengths has been done principally with ordinary photographic plates which have been specially treated with dyes to make them sensitive to these long waves. Such

dyes as alizarin, nigrosin, cyanin and dicyanin have been used for the purpose. Up to the present, however, comparatively few spectra have been investigated by this method. In most cases, photography with stained plates has not registered waves much longer than 8000 A, although it is possible to reach much longer waves by this method. Furthermore, such work has been done chiefly wwith the low dispersion of prisms or small gratings and very few long wave-lengths have been measured in International Angstroms. By using the photographic method with interferometers or with larger gratings accurate information concerning the spectra of the elements can be extended beyond 9000 A without much difficulty.

2. Purpose.

Some work on spectroscopic analysis at the Bureau of Standards led to a photographic investigation of the spectra of some of the elements in the region of the longer wave-lengths. The photographic sensitizers dicyanin and dicyanin A were used and found to be of great value in photographing spectra between the wave-length limits 5600 A to 9600 A. This work was begun with the plan of studying the longer waves of the spectra of elements commonly found in iron as impurities; such as nickel, cobalt, chromium, manganese, copper, titanium, vanadium, silicon, calcium and carbon. The success in photographing these led to the photography of the spectra of the fol-

lowing elements in addition to those of iron and its impurities: lithium, sodium, potassium, rubidium, caesium, beryllium, strontium, barium, magnesium and carbon. Thus the arc spectra of twenty of the chemical elements were photographed from 5000 A to 9000 A and beyond.

Accurate measurements of wave-lengths to 8824 A in the arc spectrum of iron have been made with interferometers by Burns[1]. Similar measurements have been made to 8210 A in the barium arc spectrum by Werner[2]. These spectra do not contain a sufficient number of evenly distributed and sharp lines in this region to recommend them as entirely satisfactory for standards. A photographic survey of the spectra of the elements may disclose a more satisfactory source for long wave standards.

Some of the spectra which were photographed, notably those of cobalt, nickel, titanium, vanadium, manganese and chromium, were found to have sharp lines whose wave-lengths can be more accurately obtained with interferometers than from the grating photographs made in this work. Furthermore, the number, distribution and intensity of lines in this part of the cobalt spectrum were found to be more satisfactory than in the iron arc spectrum.

1.) Burns. Journal de Physique p. 457; 1913. (123)
2.) Werner. Ann d. Physik. 44, 2, p. 289; 1914.

If the sharpness of these cobalt lines be examined with the interferometer, the cobalt arc may be found superior to the iron arc as a source of long wave standards. The wave length measurements in these sharp line spectra will therefore be postponed until the interferometer is applied.

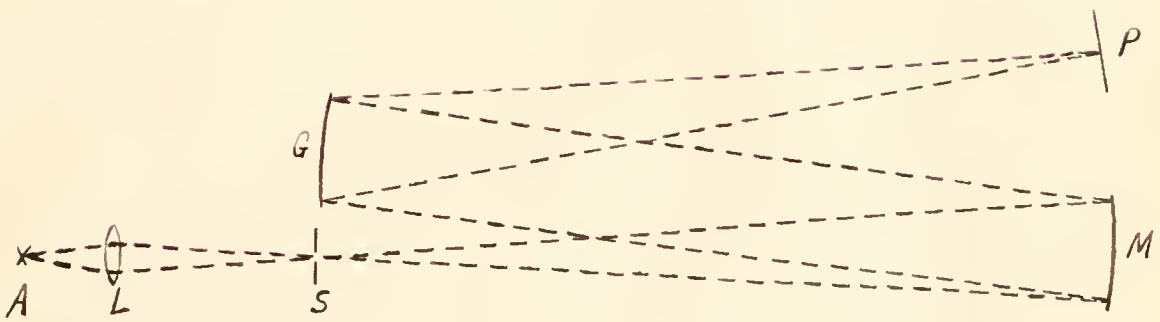
Many elements, especially the alkali metals, have spectra the greater part of whose lines are broad, diffuse, reversed or unsymmetrical. A careful study of the long-wave spectra of some of these elements has been made.

The wave-lengths have been measured in International Angstrom Units and the results are probably as accurate as the structure of the lines will permit. These result are of special interest because of the regularities and series relationships which exist in the spectra of the II and III groups of elements in the periodic table. The apparatus and method used in photographing and measuring these spectra are described in this paper and the results are given for lithium, sodium, potassium, rubidium, caesium, copper, beryllium, calcium, strontium, barium and magnesium.

3. Apparatus.

The spectra were photographed in the first order spectrum of a concave grating ruled by Dr. J. A. Anderson at the Johns Hopkins University. The grating has a radius of curvature of 640 cm and

the ruled surface is 7.5cm by 13.3 cm with 299 lines per millimeter, or 39800 lines in all. The mounting is shown in the diagram.



An image of the arc A was magnified about 3 diameters and focused by the lens L on the slit of the spectrograph. The light passing through the slit S filled a concave mirror M which sent out a parallel beam to the grating G, which was placed close beside the slit S. The grating G focused the spectra on the photographic plate P. The grating was fixed on one end of a webbed steel beam and the camera was moveable along the other end of the beam. The camera could be

rotated by sliding this end of the beam along a double track, rotation taking place about a vertical axis through the centre of the grating. The grating focused the spectra in a circle with its centre at the grating and radius equal to the focal length of the grating. This spectrograph gives a dispersion of 10 Angstroms per mm. in the first order so that a spectrum length of 2000 A could be photographed on a 20 cm. plate. The focal curve was practically plane for this distance.

After the camera was focused for a particular spectral region it was clamped to the double track. The whole apparatus was clamped to massive brick piers cemented to the thick concrete floor in a basement room where mechanical disturbances and temperature variations were small. A wooden house surrounded the entire apparatus and protected the camera from stray light.

The advantages of the grating mounted in parallel light in addition to compactness and stability, are intensity of spectra and freedom from astigmatism. The intensity given by the so-called Rowland mounting is quadrupled by this mounting in parallel light. This is of great importance for the photographing of faint spectra and in regions where specially prepared plates must be used. The stigmatism of the slit images when the grating is mounted in parallel light allows

the comparison spectrum, containing standards, to be photographed directly beside any other spectrum. This was accomplished by placing suitable diaphragms in front of the slit. An aperture was used which allowed light from an arc to cover two millimeters of the slit, and then this portion was covered and 5 mm on either side was exposed to the iron arc. The slit width was usually about 0.02 mm.

4. Sources.

Arcs were made of metallic electrodes in all cases where it was possible. In the other cases the following salts were used in Acheson graphite electrodes: $LiCO_3$, NaCl, KCl, $RbCl_2$, $CsCl_2$, $BeCO_3$, $SrCl_2$ and $BaCl_2$. For calcium and magnesium arcs the lower electrode was of the metal and the upper one of graphite.

Direct current was supplied by a potential difference of 220 volts. The current strength was made to correspond roughly to the wave-lengths to be photographed, i.e. 6 amperes were used to photograph from 6000A to 7000A, 7 amperes from 7000A to 8000A, etc. An exception was made in the case of magnesium. The metallic electrode would ignite with large currents but burned quite satisfactorily with 3 amperes and 110 volts. Electrodes of Norway iron were used for producing the light of the comparison spectrumand the arc was operated under standard conditions.

In every case, only light from the center of the arc was photographed, the light from the electrode being screened from the slit by the diaphragm.

There is an important difference between so-called chemically pure substances and substances which are spectroscopically pure. The greatest skill and care of chemists seems unable to produce elements in an absolutely pure state. The use of impure materials for sources has naturally led to frequent mistakes in assigning spectrum lines to the proper element. Some of the long waves which have been wrongly identified by others will be pointed out in the results of this work. It is possible that some errors of this kind still remain.

Spectroscopic analysis of the Acheson graphite showed the presence of sodium, calcium and barium. All the lines photographed were measured but the wave-lengths due to impurities were separated from the others and will be found in Table II. This shows the impurities in the "chemically pure" salts used in this work.

When large quantities of salts are used in graphite electrodes the spectrum of carbon is quite effectively suppressed. If only small quantities are used the thousands of lines due to carbon become very troublesome. Electrodes of copper cored and filled with salt may be recommended for work in the region of long wave-lengths for

the copper spectrum has very few strong lines in this region.

5. Photography of Red and Infra-Red Spectra.

Among the various photographic sensitizers which have been used to photograph red and infra-red spectra, the most efficient and convenient is probably dicyanin. Eder[3], Geiger[4], Burns[5], and others have used is successfully and it is regretable that its use has not become more universal.

Photography with stained plates is generally thought to be difficult, troublesome and uncertain. Perhaps some have tried dicyanin without success because their dye was inferior or worthless. This dye is quite easily decomposed by the action of light or heat after which its value as a photographic sensitizer is lost. If stored in a cool, dark place it may be kept for months without decomposing. The process of staining plates is probably thought to require special apparatus and technique. It is possible, however, to obtain satisfactory results with a very simple procedure.

The most efficient staining bath was found to be the one recommend by Dr. Burns[6]. It consisted of a mixture of water, alcohol,

3). Eder, Kaiser. Akad. d. Wiss. p. 2289, 1914.
4). Geiger, Ann. d. Phys. 39, p. 752, 1912.
5). See Note I.
6). See Note I.

ammonia and dicyanin in the following proportions: About 4 cc of a stock solution of 1 part dicyanin to 1000 parts of alcohol, were added to 50cc distilled water, 50 cc ethyl alcohol and 5cc of strong ammonia. Ordinary photographic plates like Seed 27 or Graphlex were soaked in such a bath from three to five minutes, rinsed in alcohol 30 seconds and dried by a current of air from an electric fan. Plates treated in this manner were found to be quite sensitive to wave-lengths between 6000A and 9000A. The strong lines between 7500A and 8500A in the spectra of the alkali metals were photographed with exposures of one minute or less. In the barium arc spectrum a line of wave-length 9370A was registered with an exposure of 20 minutes, while an exposure of 60 minutes on a plate stained with dicyanin A showed the line of wave-length 9608A quite strongly (See plate No. V.). The exposures were usually limited to 30 minutes in length so as to be reasonably sure that no displacements had taken place in the spectrograph. With these half-hour exposures the spectrum of the iron arc was photographed to 9118A, the chromium arc to 9290A, the vanadium arc to 9087A, the nickel arc to 8968A, the cobalt arc to 8926A, and the titanium arc to 8734A. In the region 5600 A to 7600 A the exposure times ranged from one to fifteen minutes.

A few typical spectrum photographs as made with the dicyanin stained plates are reproduced in the plates I,II,III,IV, and V. These

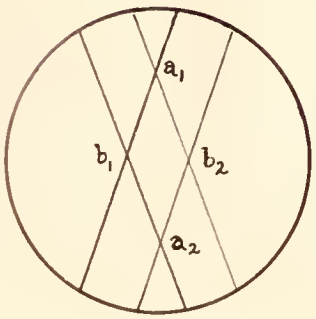
photographs are enlargements of three diameters made from copies of the original spectrum plates. They show the first order spectrum of some element bounded on either side by the arc spectrum of iron as photographed in the second order. An exception to this arrangement is found in the first two spectra on plate I. In these cases the first order spectrum of iron is shown above that of caesium. The wave lengths of the strong lines in the middle spectrum are indicated by the accompanying numbers.

6. Wave-length Measurements.

The plates were measured with the excellent measuring machine at the Johns Hopkins University. This machine has a screw which is nearly perfect throughout its entire length of more than 50 cm. The pitch of the screw is 1 mm. The head has a diameter of 25 cm and the circumference is divided into 1000 parts. One division thus corresponds to 1μ along the axis of the screw or to 0.01 A on a spectrum photograph with 10A per mm.

Turning the head moved the microscope along ways which were parallel to the screw. The spectrum plate was clamped firmly to a shelf fastened to the ways. A 5-fold magnified image of a part of the plate was then visible in the field of the microscope with the cross-hair images superposed. The microscope contains two pairs of

cross-hairs as shown in the diagram. Readings were made when the



cross-hair intersection b_1 was on a spectrum line and again when b_2 was on the same line. The mean of these two readings was used for the position of the line on the plate. The positions of the standards in the comparison spectrum of iron were obtained from readings when the cross-hair intersections a_1 and a_2 were on the lines. After the two spectra were completely measured from short to long wave-lengths, the plate was reversed and remeasured from long to short wave-lengths. Thus each determination of wave-length is based upon four independent observations of the position of a line with respect to the neighboring standards.

The scale of the plate, assuming normal dispersion, was obtained by dividing the difference in wave-length by the measured distance between the first and last standards measured on the plate. All the other measurements were then reduced to wave-lengths on this basis. The deviations from standard values of the values thus obtained for the iron lines were plotted as a function of wave length and a curve was drawn through these points. From this curve the correction required to express any other wave-length on the International scale was obtained.

Interference measurements of wave-lengths in the iron spectrum by Burns, Meggers and Merrill[7] were used as standards. These standards contain the 85 International secondary standards from 3233A to 6750A together with 318 other iron lines compared with the International standards by the interferometer method. This set of standards contains chiefly the sharpest iron lines of different intensities consistent with quite regular distribution through the spectrum. The average distance between these standards is less than 9A. Eighty-six percent of the 85 International secondary standards are lines of intensity 4 to 6 inclusive while only 47% of the additional 318 lines have these intensities, the remainder being distributed among fainter and stronger lines. These facts make this set of standards very convenient for the measurement of wave-lengths.

The comparison iron spectrum from 3300A to 4800A was usually photographed in the second order of the grating when long waves from 6600A to 9600A of other spectra were photographed in the first order. The first order spectrum of iron was photographed besids the shorter waves of the other spectra. On a few plates the first order spectrum of iron was used to 8600A and Burns' values were then used for the standards longer than 6750A.

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7). Bull. Bureau of Stand. 13, p. 245, 1916.

7. Results.

The results are contained in the following tables and remarks. The first column of each table gives the wave-lengths as measured in International Angstroms; the second column indicates the intensity and character of each line. The strongest lines are called intensity 10. Faint but measurable lines are called intensity 1. The character of the appearance of a line is represented by letters which have the following meanings:

b = broad
d = perhaps double
h = hazy
H = very hazy
l = shaded to red
L = much shaded to red
R = broadly reversed
ra = narrow reversal, red component stronger.
Sb = very broad.

The third column indicates the probable error of the measurements of each wave-length. The letters have the following significance:

A = probable error .000A to .010A
B = " " .010A to .020A
C = " " .020A to .030A
D = " " .030A
E = only one determination.

A and B also indicate that the line was measured more than twice. In fact most of the stronger lines were measured on three to six plates. The long lines marked E are generally faint and show only on the longest exposures. Their wave lengths are not very accurate but they are all included in the table to show how many of them have been recorded by comparatively short exposures of the dicyanin stained plates.

In the following tables I.A. indicates that the wave lengths are given in International Angstrom units. The others are based on Rowland's system of standards.

The tables also contain the results of others who have photographed in this region with stained plates. The only investigations of this kind embracing more than one spectrum are these of Lehmann[9], Hermann[10], Saunders[11], Lorenzer[12] and Eder[13]. Among these, Eder's results are the only ones expressed in International Angstrom units. Lorenzer used the Hartmann[14] values for the iron lines as standards. For purposes of comparison, the results based upon Rowland's standards may be changed to the International scale by subtracting the following quantities:

	0.22A	from	5500 to 6050
	0.21"	"	6050 to 6500
	0.22"	"	6500 to 6570
	0.23"	"	6570 to 6750
	0.24"	"	6750 to 6850
	0.25"	"	6850 to 7000
	0.26"	"	7000 to7200
	0.27"	"	7200 to 7400
	0.28"	"	7400 to 7700
	0.29"	"	7700 to 8000
	0.30"	"	8000 to 8200
	0.31"	"	8200 to 8300
about	0.35"	"	8300 to 8800

For the proper discussion of series relationships among the lines

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9). Lehmann. Ann d. Phys. (4) 5, p.633, 1901, strong line I, weak line 4
10). Hermann. Ann d. Phys. (4) 16, p. 684, 1905.
11). Saunders. Astrophys. Jl. 20, p. 188, 1904
12). Lorenzer. Dissertation, Tubingen, 1913.
13). Eder. Sitzungsber. d.k. Akad. d. Wissensch. Wien, p. 2289, 1914.
14). Hartmann. Physik. Zeitschr. 10, p. 123, 1909.

in these spectra , the wave length should be reduced to vacuum. This cannot be done accurately at the present time because the dispersion of air has never been determined for waves longer than 6800A. For this reason an investigation on atmospheric dispersion in the region of long wave lengths has been begun. The frequency differences of pairs of lines which appear in doublet series in some of the spectra will not be affected appreciably by the dispersion of the atmosphere. Such frequency differences as determined from my wave length measurements will be given below.

Comparison with the tables of solar wave-lengths, published by Capt. (Sir) W. de W. Abney,[15] brings out certain interesting facts. Aside from the telluric lines, a large percentage of the rays in the infra-red solar spectrum are due to iron, as would be expected from the character of the solar spectrum in the visible and ultraviolet regions. The strongest solar lines in the infra-red are due to calcium and magnesium. These are the lines X_{I}, X_{II}, X_{III}, and X_{IV} of Abney, the last, the weakest, being due to magnesium. Some of the strong lines of barium seem to show in the solar spectrum as well as the strong lines of potassium (7664 and 7699), sodium (8183 and 8194), lithium (8126) and copper (7933). Many of Abney's wave-lengths are in error by several tenths of an Angstrom, and further identification of these Fraunhofer lines with elements in the sun is uncertain and

15. Phil. Trans. 177, p. 457, 1886.

difficult. I have now photographed the solar spectrum from 6800A to nearly 10000A, on dicyanin stained plates, and hope that the wave-lengths measurements will make more identifications possible.

Table I.

Lithium.

Meggers. IA			Eder IA		Saunders	Lehmann	Kayser &Runge[16]	
6103.53	10b	E					6103.77	10R
					6240.3			
6707.85	10R	B	6707.85	100R			6708.2	10R
8126.52	10	B	8126.27	10b	8127.0	8127.34 1		

The arc was produced between graphite electrodes containing lithium carbonate. The impurities present were sodium, potassium, calcium and barium.

The resemblances of the spectra of the alkali metals have attracted much attention to them. They all contain definite sequences or series of lines, and the members of each series possess the same spectral character. In general three types of series exist in each of these spectra. The intense and easily reversed lines constitute the so-called principal series. Most of the other lines are broad and diffuse. They may be arranged in two subordinate series, the lines of the first subordinate series being broadened by shading toward the red. In the spectra of sodium, potassium, rubidium and caesium all the series

16. Kayser & Runge. Wied. Ann. 41, p. 302, 1890.

consist of doublets but the lines in the lithium spectrum have generally been measured as single. The lines are no doubt very narrow pairs and King[17] has recently found the line 6707 double under certain conditions. Two components for this line have also been observed by others. The separation is about 0.15A.

Table 2.

Sodium.

Meggers IA			Eder IA			Kayser & Runge[18]		Saunders	Hermann	
5682.97	8	E				5682.90				
88.61	10	E				88.26				
5889.97	10R	E				5890.10				
95.94	8R	E				96.16				
6154.40	4	E				6154.52				
60.96	5	E				61.15				
								7369.4		
								77.4		
								7410.0		
						Lehmann.		18.3		
8183.30	8rs	C	8183.35	10OR		8184.33	1	8184.5	8183.74	2
									8188.17	0
8194.82	10rs	C	8194.92	10OR		8194.96	1	8196.1	8196.33	3

Sodium chloride was used in graphite electrodes for the arc. The impurities present were potassium, strontium, lithium, calcium and barium. When a large amount of sodium chloride was used in the arc the long lines 8183 and 8194 showed narrow reversals displaced from the centers of the lines towards shorter wave lengths. The wave-lengths given are from measurements on these reversals. When unre-

17. King. Astrophys. Jl. 44, p. 169, 1916
18. Kayser & Runge, Wied. Ann. 41, p. 302, 1890.

versed the lines are shaded to the red and the measured wave-lengths are then usually from 0.1A to 0.2A larger. These two lines are the first pair of the first subordinate series and their frequency difference is 17.2, which is identically the frequency difference of the first pair of the principal series, 5889 and 5895. The lines 6154 and 6160 are the first pair of the second subordinate series, and their frequency difference from these measurements is 17.3. The frequency difference for the second pair (5682 and 5688) in the first subordinate series is 17.4. The number of waves per centimeter ranges from about twelve thousand to about seventeen thousand for these wave-lengths. Hence the greatest range in frequency differences of these four pairs of lines is little more than one part in 100,000 in the actual wave number, and the deviations from constancy are of the same order of magnitude as the errors in measurement.

Table 3.

Potassium.

Meggers	IA		Eder	IA	Kayser & Runge[19]		Saunders	Hermann	Lehmann.
5782.50	2h	E			5782.67	5u R			
5801.96	4h	E			5802.01	6u R			
12.52	1h	E			12.54	6u R			
5832.09	2h	E			5832.23	7u R			
6911.30	10	A	6911.31	5	6911.2	7	6911.8		
38.98	10	A	39.07	6	38.8	8	39.5		
							6966.3		
7664.94	10R	A	7664.95	15CR	7665.6	10u R	7664.91	7665.29 8	7668.54 10
99.01	10R	A	99.02	100R	99.3	10u R	99.08	99.32	7701.91 10
							7931.8		

19). Kayser & Runge. See Note 16

Potassium chloride was used in graphite electrodes. The impurities in the spectrum were sodium, rubidium, calcium, barium and lithium. The lines 7699 and 7664 are the first pair of the principal series and their frequency difference from these measurements is 57.74. The next pair, 6938 and 6911, are the first lines of the first subordinate series. Their frequency difference is 57.72, or identically that of the first pair of the principal series. The lines 5801 and 5782 are the second pair in the first subordinate series and their frequency difference is 57.71. The pair 5832 and 5812 belong to the second subordinat series. The difference in waves per cm for this pair is 57.73. The above measurements thus give exactly the same frequency difference for these four pairs.

Table 4.

Rubidium.

Meggers.	IA		Eder	IA	Eder & Valenta[20]		Saunders	Lehmann.	
6070.95	21	E			6071.30	1	6071.1		
6159.84	51	E			6160.20	2	6160.0		
6206.48	81	E			6206.74	3	6206.7		
98.50	101	E			98.85	5	98.8		
					7060.09	1			
7280.22	101	C			7280.53	1	7280.2	7277.01	3
7408.37	101	C	7408.49	11	7409.71	1	7408.5	7406.19	3
7619.12	81	C	7619.17	2b	7619.7	1	7619.2	7626.66	6
7757.80	81	B	7757.70	2b			7757.9	7753.58	6
59.58	1	C			7759.6	1	59.5		
7800.29	10R	A	7800.30	10OR	7800.3	4R	7800.2	7805.98	10
7947.64	8R	A	7947.63	50E	7947.7	2R	7947.6	7950.46	8
			8521.21	3u				8513.26	4

20). Eder and Valenta, Atlas Typischer Spectren, Wien, 1911.

Rubidium chloride was used in graphite electrodes. The arc spectrum showed sodium, potassium, caesium, calcium, barium and lithium as impurities.

The line 7060 observed by Eder and Valenta is due to barium. The line measured as 8521 by Eder and 8513 by Lehmann belongs to caesium.

The lines 7947 and 7800 are the first pair of the principal series. Their frequency difference is 237.7. Lines 7757, 7619 and 6298, 6206 are the first two pairs of the first subordinate series. Their frequency differences are 234.5 and 235.4. Lines 7408, 7280 and 6159, 6070 are the first two pairs of the second subordinate series. Their frequency differences are 237.5 and 237.7. Thus it appears from these measurements that the frequency differences of pairs in the second subordinate series are identical with that of the first pair of the principal series, while those of the first subordinate series are about one percent smaller. This is also true for the succeeding pairs.

Table 5.

Caesium.

Meggers	IA		Eder	IA	Lehmann		Saunders.
5663.79	H	D					
5844.7	H	D					
6010.33	7b	C					
							6034.8
6212.87	8b	C					6213.1
6217.27	1b	C					6217.6
							6355
6354.98	4h	C					6355.3
							6359
							6434
							6475
							6587.3
6586.94	51	D	6587.11	61			6588.0
							6630.5
6723.18	10b	A	6723.28	20			6723.7
							6826.9
							6872.6
73.17	10b	A	73.35	20R			6973.1
6983.37	5b		6983.39	3b			6983.8
7228.5	L	E			7227.46		7228.8
7279.7	L	E					7280.5
7609.13	5b	B	7609.28	21	7616.58	3	7609.7
			7800.11	2b			
7944.11	6b	C	7941.1	1u			7944.7
8016.2-9	10L	D			8019.62	3	8001.7
8079.1-8	10L	D			8082.02	3	
8521.12	10R	A			8527.72	1	
8761.35	5b	B			8766.10	2	
8943.46	8R	A			8949.92	2	
9172.23	2b	A			9171.38	3	
9208.40	1b	A			9211.86	3	

Caesium chloride was used in graphite electrodes. The arc spectrum contained sodium, potassium, rubidium, lithium, calcium and barium as impurities. The line 7800 measured by Eder is due to rubidium. The line 8079 and the line 8016 are very unsymmetrical. The photographic maximum is therefore dependent on the duration of the exposure for its position and the measurements on this maximum vary between the limits indicated.

The following lines belong to series:

		Meggers	Kayser
8943.46 8521.12	First pair of principal series	554.1	546.9
9208.40 8761.35	First pair of first subordinate series	554.2	552.0
6973.17 6923.18	Second " " " " "	553.2	533.8
6212.87 6010.33	Third " " " " "	542.2	543.0
5844.7 5663.8	Fourth " " " " "	546.5	547.0

Kayser[21] suspected that accurate measurements would show these frequency differences to be constant. Although my measurements show the frequency differences to be identical for the first pairs of the principal and subordinate series, the frequency differences for the next three pairs of the first subordinate series show the same deviations from constancy as the older measurements.

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21). Kayser, Handbuch der Spectroscopie. II, p. 529.

Table 6.

Copper.

Meggers	IA		Aretz[22]		Hasbach[23]	
6415.18	1	E	6415.155	1		
27.57	1	A	27.564	2		
			52.287	0		
			56.672	1u		
74.20	3	A	74.176	5u	6474.2	1u
85.18	2	D	85.142	5u		
			6504.051	0	6485.15	1
			06.142	2u		
			31.437	1		
6544.51	1h	D	44.427	2u		
50.98	1	E	50.977	3		
65.54	3h	C	65.555	2u		
			83.542	2u		
			99.681	5		
6621.61	4	A	6621.623	1u	6621.59	1
29.67	1	C	29.730	1u		
72.23	3	A	72.234	5	72.2	1u
6741.42	7	A	6741.418	6	6741.4	1u
49.29	2b	E				
75.64	2b	C	81.869	ou		
6821.86	1h	C				
35.46	1	E				
40.99	1h	A				
81.94	2	A				
89.92	2	C				
90.90	2	A				
6905.90	6	A	6905.937	3u		
20.09	4h	A	20.287	1u		
35.80	2h	B				
68.36	1	C				
7000.02	1h	E				
39.34	3	B				
7124.66	1	E				
54.29	1	E				
93.56	2h	A				
7427.26	1	E				
7570.09	5	A				
71.98	4	A				
74.18	3	A				
75.41	2	A				

22). Aretz. Zeitschr. f. wiss. Phot. 9, p. 256, 1910.
23). Hasbach. " " " " 13, p. 399, 1914.

Copper. (Continued

Meggers.	IA	
7848.55	1	C
7911.95	1	C
33.20	10	A
54.23	2	B
8006.27	2	B
17.78	2	B
71.06	2	C
92.74	10	B
8114.17	2	B
78.96	2	B
87.90	1	E
8216.22	1	E
23.13	1	E
42.27	1	E
73.45	1	E
8408.00	1h	E
46.40	2	B
8680.08	1	E
83.17	1	E

Copper rods 6 mm in diameter were used as arc electrodes. The D lines of sodium appeared in the spectrum. The work of Aretz and of Hasbach should be consulted for wave-lenghts shorter than 6621A. Aerta made exposures on Wrattan & Wainwright plates for six hours and obtained lines below 6621A which were not recorded by the fifteen minute exposures on my plates. The line 6599 which Aertz marked intensity 5 did not appear on my plates. It may represent an impurity.

The copper arc spectrum also has a doublet system of series. The first pair of the principal series, 3247.550A and 3273.967A according to Hasbach, has a frequency difference of 248.45. Lines 7933.19A and 8092.76A are the first lines of the second subordinate series and have a frequency difference of 248.55. The lines 5133.261 A

and 5220.083A have a frequency difference of 248.40. This pair belongs to the first subordinate series. The frequency differences of these three pairs representing three different series differ from each other by less than one part in 100,000 in the wave number.

Beryllium.

Investigations in the arc spectrum of Beryllium have thus far disclosed only twelve lines with certainty. The longest of these has a wave-length of 4572.A, which is in the blue part of the spectrum. Exposures of half an hour on my stained plates showed no traces of lines between 4572.A and 9000A. Beryllium carbonate was used in graphite electrodes to produce the arc spectrum.

Table 7.

Strontium.

Meggers	IA		Eder	IA	Hampe[24]	IA	Lehmann		Eder & Valenta[25]	Lorenser.	
6363.98	4	C			6363.932					6364.19	5
70.00	5	C			69.959					70.18	6u
80.77	5	C			80.740					80.94	10e
86.57	7	C			86.507					86.76	9u
88.32	6	D			88.245					88.48	6u
6408.49	9	C			6408.455					6408.69	15
46.70	1	C			46.676					46.91	3
65.78	1	C			65.788					66.10	2
6504.02	5	C	6504.01	6	6503.990		6504.07	1	6504.26	6504.26	12u
										16.07	1
										21.53	1
46.82	4	B	46.79	4	46.785		46.27	4	47.09	47.06	8u
50.28	5	B	50.29	6	50.253		50.19	3	50.53	50.51	12u
6617.28	5	B	6617.27	4	6617.268		6616.92	3	6617.50	6617.54	10u
43.56	4	A	43.52	3	43.545		44.05	3	43.78	43.80	6u
							6708.10	4			
							54.21	4			
										6769.59	1
6791.08	5	A	6791.06	6	6791.046		6792.19	1	6791.30	91.35	10
										6803.55	1
6878.36	10	A	6878.36	7	6878.347		6880.69	1	6878.63	78.65	15v
92.62	6	A	92.62	4	92.598		93.37	3	92.83	92.86	8s
7070.15	10	A	7070.13	20R	7070.102		7070.34	2	7070.45	7070.53	20v
										88.90	1
7153.08	4	A	7153.07	2					7153.24	7153.43	4s
67.24	6	A	67.29	5			7168.02	3	67.49	67.66	10u
7232.34	6	A	7232.30	4			7232.10	3	7232.53	7232.56	8u
							54.44	3			
7287.44	1n	E	87.57	1						87.75	4
			89.25	1						89.19	2
7309.47	6	A	7309.46	10					7309.65	7309.70	12u
										48.72	1
										62.83	1
										7406.07	2
			7408.13	1						08.22	2
										38.53	2
7621.54	5	A	7621.55	3						7621.76	8
73.11	6	A	73.07	6						73.38	10
			8182.58	4							
			95.14	4b							

24). Hampe. Zeitschr. f. wiss. Phot. 13, p. 348, 1914.
25). Eder & Valenta. See Note 20.

Strontium chloride in graphite electrodes was used for the arc. Lithium, sodium, calcium, and barium were found as impurities. The lines 8183 and 8195 observed by Eder are due to sodium. The unsymmetrical character of these two lines makes their measured wave-lengths several tenths of an Angstrom larger than when measurements are made on the reversals. The line 6708 measured by Lehmann is probably a lithium line. The line 7408 measured by Eder and by Lorenser may belong to rubidium.

Table 8.

Calcium.

Meggers	IA	Eder	IA	Crew & McCauley [26]	IA	Holtz [27]	IA	Lehmann		Lorenser.	
6439.13	10 E			6439.086	9	6439.061				6439.31	20v
49.83	5 E			49.811	7	49.794				50.05	10
55.60	3 E			55.606	3	55.560				55.82	8s
62.62	10 E	6462.55	8	6462.576	9	62.550				62.82	20v
										64.93	2u
71.69	5 E	71.64	5	71.659	5	71.644				71.92	10
93.83	7 E	93.77	7	93.789	8	93.762				94.04	20v
99.67	5 E	99.64	5	99.648	4	99.624				99.94	10
				6508.742	1			6508.02		6509.10	
6572.78	2 E	6572.78	4	6572.783	3	6572.71		6571.93	2	6573.03	6s
										6656.1	1u
								6666.98	2	65.6	1u
		6707.88	2	6707.866	1	6707.81				6708.06	6u
										10.12	1
6717.78	8 C	17.69	8	17.688	5	17.70		6714.47	3	18.01	15v
										44.0	1u
										47.2	1u
								67.02	1		
								82.85	4		
										84.13	4u
										89.38	1
										98.75	3u
								6833.50	4		
										6866.80	1u
										84.29	2

26). Crew & McCauley. Astrophys. Jl. 39, p. 29, 1914.
27). Holtz. Zeitschr. f. wiss. Phot. 12, p. 101, 1913.

Calcium (continued).

Meggers	IA	Eder	IA	Crew & McCauley	IA	Hermann	Lehmann		Lorenzer	
7148.15	10 B	7148.14	6	7148.123	3		7146.45	3	7148.49	15v
7202.21	8 A	7202.15	4	7202.161	2		99.83	1	7202.51	15v
7326.12	8 A	7326.10	5	7326.099	1		7322.95	2	7326.43	20v
									7468.69	3
									7521.22	1u
									34.75	2u
									66.08	3u
									92.39	1
									87.79	2
									98.40	3
							7600.74	4u		
									7602.78	4
									10.66	6
							12.34	4u		
									45.25	1u
									7984.25	1u
									95.31	2u
8153.13	1 E								8153.13	2
8497.98	8 B	8498.11	4			8492.32	00 8499.20	3	8498.35	3
8542.06	10 B	8542.25	1u			8542.48	1 8543.08	1	8542.47	5
8662.10	9 B					8662.42	0 8662.10	2	8662.50	3

An electrode of metallic calcium was used below and a graphite electrode above to produce the arc. Sodium, lithium, potassium and strontium contaminated the spectrum. The line 6707 measured by Eder, Crew & McCauley, Meltz and Lorenser is due to Lithium although Eder insists that it is a calcium line. Woodward[28] has shown that this line is absent in the arc spectrum of pure calcium. By means of a 25 ampere arc and longer exposures Lorenser has found a number of new lines. Some of these may belong to band spectra and to impurities. Most of the lines become broad and unsymmetrical when the arc is operated with large currents. Crew and McCauley used the arc in a vacuum to get sharp lines.

28). Woodward. Astrophys. Jl., 41, p. 169, 1915.

Table 9.

Barium.

Meggers	IA	Lorenser	Eder	Burns [29]	IA	Werner [30]	IA	George [31]	IA	Hermann
7610.50	3 A	7610.83	8ss	7610.46	2			7610.472		7610.74
		16.83	1u							
36.88	2 B	37.29	15u R	36.89	2			36.875		37.47
42.92	5 B	43.31	20u R	42.88	3	7642.37	7642.815			43.43
		62.31	3							
72.12	7 B	72.48	20v	72.10	5	72.10	72.104	72.093		72.42
7706.58	3 C	7706.88	8v	7706.59	2					7706.82
										09.56
21.77	1 E	22.13	4u R							
51.69	2 C	52.02	8u V	51.74	2					51.92
66.80	2 C	67.19	4u R	66.81	5					
75.37	1 E	75.74	3u R							
80.49	8 A	80.77	12	80.50	5	7780.50	7780.497	7780.503		80.70
98.24	1 E	98.65	2							
		7829.25	2							
7839.56	2 B	39.82	8u	7839.56	3	7839.58		7839.579		7839. 57
		63.74	1u							
		65.51	1u							
78.93	2 B	78.34	3u R							78.13
7905.80	7 B	7906.12	15	7905.77	6	7905.77	7905.770	7905.771		7906.13
11.36	6 B	11.67	8	11.35	5	11.34	11.353	11.325		11.53
39.42	1 E	39.79	2u							39.21
		57.61	1u							
61.20	1 D	61.47	2u							61.23
82.42	1 C	82.75	3u							
8018.21	1 C	8018.64	2							
8120.44	2 B	8120.88	4							8120.84
47.75	3 B	48.14	3							48.32
58.11	1 D	58.56	2u							
61.55	2 D	62.09	2u							
8210.28	10B	8210.65	10u	8210.53	5	8210.32		8210.327		8210.71
24.23	1 E									
59.93	1 E							Lehmann		
63.97	2 E	64.30	1u					8259.94	4	
84.53	2hC							89.08	3	
		88.41	1u							
8325.34	2hB							8328.26	4	
		8329.17	3u							
50.64	1 E									
90.38	1 E									
8414.52	1h E									
8514.23	1h C	8514.50	1u					8518.24	4	
21.91	1 C									
		42.72	1u							

29). Burns. Kayser's Handbuch der Spectroscopie Vol. VI, p. 904
30). Werner. See Note 2.
31). George. Zeitschr. f. wiss. Phot. 12, p. 237, 1913.

Barium. (continued).

Meggers	IA		Lorenser		Eder	IA	Lehmann		Hermann.
8559.90	10	A	8560.21	6u	8559.98	5	8563.32	1	8560.20
67.53	3h	B	68.09	3					
69.11	1	E	69.60	2					
			70.34	1					
82.04	4	B	83.66	3u			85.70	4	
93.40	1	E							
8654.02	4	B	8654.40	3			8659.38	4	8654.33
			59.65	1					
8710.74	1	A							
37.71	1	C							
99.70	2h	C					8806.22	4	8799.86
8860.96	4	B	8861.32	2			8868.50	4	8861.40
8914.96	4	A	8915.40	2			8921.04	3	8915.19
27.30	1	E							
37.85	1	E							
9091.15	1	E							
9183.70	1	E							
89.43	2	E							
9219.65	2	E							
9303.09	1	E							
24.53	1	E							
70.05	3	B							
9455.94	1	E							
9608.83	1	E							

The arc was operated with barium chloride in graphite electrodes. Lines belonging to sodium, lithium, potassium, strontium and calcium appeared in the spectrum. The line 9370 was registered by the phosphoro-photographic method by Lehmann[32], who measured the wave-length as 9367A. The line 9608 was detected by Randall[33] with a thermopile and this wave-length was given as 9610.7A. Randall measured a line of wave-length 9527.3A which did not appear on my plates.

It is unfortunate that the line structures and wave-lengths in the barium spectrum are so sensitive to the conditions under which the arc is

32). Lehmann. Ann d. Phys. 39, p. 53, 1912.
33). Randall. Astrophys. Jl. 34, p. 1, 1911.

produced. Werner used the arc in a vacuum in order to obtain sharp lines. Under atmospheric pressure many of the lines begin to broaden. Lorenser used large quantities of barium chloride in a carbon arc fed by 30 amperes. Under these conditions nearly all of the lines are broad or unsymmetrical.

Table 10.

Magnesium.

Meggers	IA		Nacken[34]	IA	Lorenser		Hermann.	
5528.49	10	B	5528.466	5				
5711.14	5	B	5711.127	1				
82.10	1	E						
6021.70	1	C						
6318.5	2b	D			6318.55	2u R		
					18.92	2u		
					19.08	1u		
					32.48	2s		
					47.27	4u		
					6457.03	1		
					64.51	2		
					6505.62	2		
					45.66	2u V		
					46.77	5u R		
7657.5	1h	D			7656.46	3		
8806.75	5	B			8807.20	5	8800.96	9
							8929.35	2
							9224.44	oo

Metallic magnesium was used as a lower electrode and graphite as an upper electrode in the arc. It was difficult to burn such an arc in air because of the tendency of the magnesium to ignite and oxidize. Lorenser burned the arc in a vacuum.

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34). Nacken. Zeitschr. f. wiss. Phot., 12, p. 54, 1913.

Table 11.

Wave-lengths of lines due to Impurities.

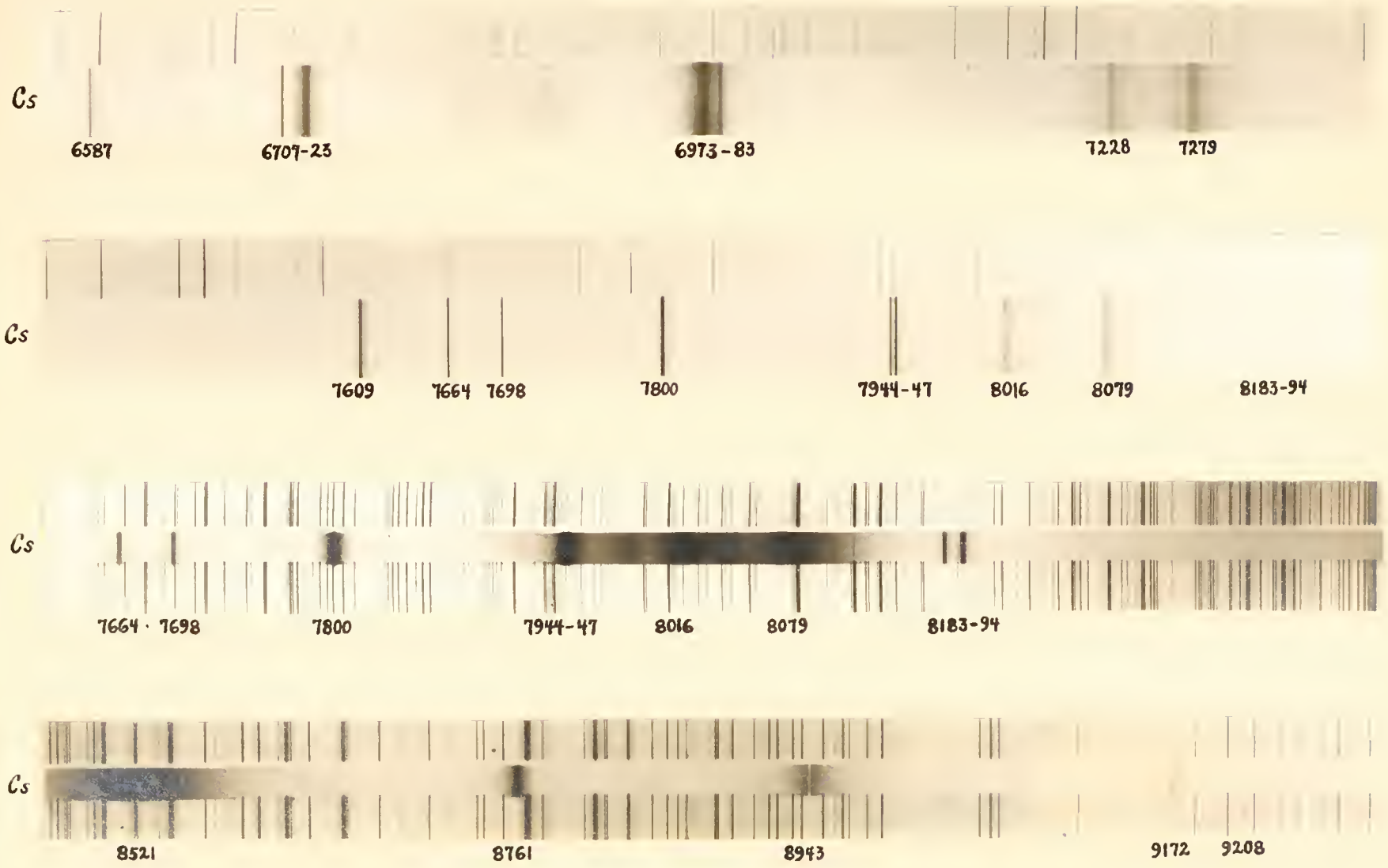
			Li		Na		K		Rb	
Li	6707.85	10R			85	2 A	81	4 A	80	8 E
Na	5889.97	10R	96	3 E			96	10 E	98	10 E
	95.96	8R	92	2 E			93	8 E	98	8 E
	8183.30	8R					49	4 D	26-56	
	94.82	10R	88	1 E			95.06	5 D	4.95-5.14	
K	7664.94	10R	91	3 A	92	5 B			93	10 A
	99.01	10R	98.95	3 A	98.98	4 B			98.98	8 A
Rb	7800.29	10R					32	2 B		
	7947.64	8R					64	1 B		
Cs	8521.10	10R							09	3 E
Sr	7070.16	10			12	2 E				
Ca	6102.78	6			70	1 E	75	1 E	76	2 E
	22.30	8	26	2 E	22	2 E	26	3 E	26	3 E
	62.30	10	20	2 E	14	2 E	18	3 E	21	4 E
	6439.13	10	07	2 E	08	2 F	10	2 E	11	3 E
	62.62	10	56	2 E	56	1 E	55	1 E	59	3 E
	93.87	7	78	1 E	78	1 E	80	1 E	82	1 E
	7148.15	10	16	2 E	15	3 A	17	1 C	14	1 A
	7202.21	8	16	1 E	16	2 C	23	1 E	15	1 E
	7326. 12	8			12	2 E				
	8497.98	8	90	1 E						
	8542.06	10	09	2 E			07	1 E	01	1 E
	8662.10	9	15	1 E			08	1 E	07	1 E
Ba	6141.75	10	75	1 E	68	1 E	70	1 E	73	2 E
	6496.93	10					99	1 E	92	1 E
	7059.94	10	94	1 E	94	1 B	94	1 B	92	1 A
	7280.29	10			30	1 E				

Table 11 (continued)

Wave-lengths of lines due to Impurities.

			Cs			Sr			Ca			Ba			Mg		
Li	6707.85	10R	84	8	A	83	1	E	82	4	A	84	2	A	75	1	A
Na	5889.97	10R	97	10	C	90.01	4	E	90.00	8	E	97	2	C	97	3	C
	95.96	8R	96	8	C	94	3	E	97	6	E	94	2	C	95	2	C
	8183.30	8R	40.	1	A				32	1	E	2	1	E	34	1	E
	94.84	10R	98	1	B				91	1	E	9	2	E	90	1	E
K	7664.94	10R	94.	8	A				92	1	C	92	2	A	9	1	D
	99.01	10R	8.99	6	A				98.99	1	C	98.99	2	A	8.9	1	D
Rb	7800.29	10R	34	10	A												
	7947.64	8R	67	4	A												
Sr	6406.49	9										44	1	E			
	6878.36	10							40	2	E	39	2	E			
	7070.16	10							17	1	E	16	2	C			
Ca	6102.78	6				77	1	E				76	1	E			
	22.30	8	23	2	C	28	3	E				26	1	C			
	62.20	10	16	3	D	23	4	E				20	2	A			
	6439.13	10	13	1	A	10	1	C				07	2	C			
	62.62	10	57	1	E							57	2	C			
	93.87	7				84	1	E									
	7148.15	10	10	1	E	23	1	E				16	2	B			
	7202.21	8				22	1	E									
	8497.98	8										95	1	C			
	8542.06	10	08	1	E							07	4	B	03	1	E
	8662.10	9	13	1	E							12	2	A	11	1	E
Ba	6141.75	10	71	1	E	77	2	E									
	6496.93	10				92	1	C									

PLATE I.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Cs
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8016
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8183-94
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9208

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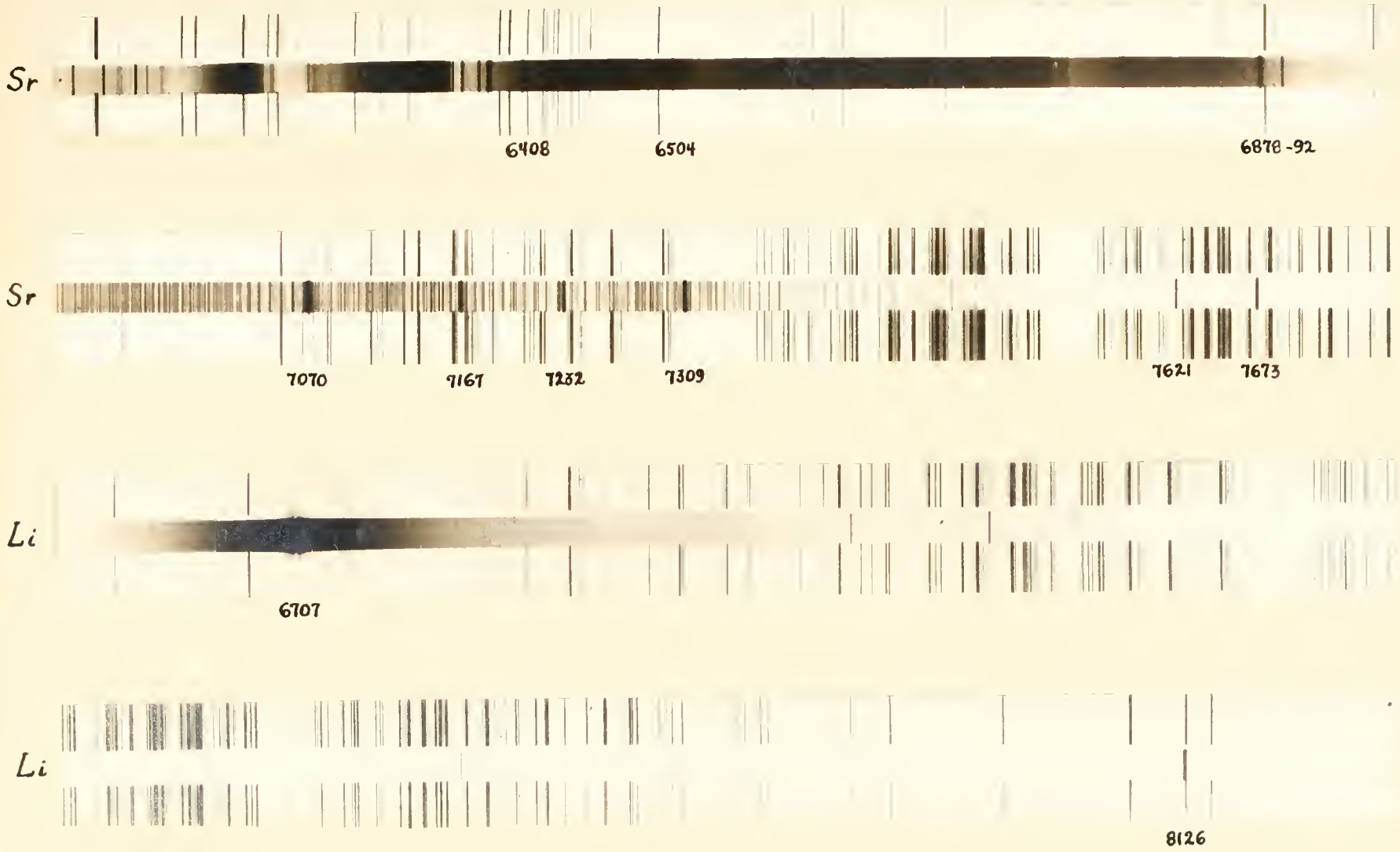
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Li
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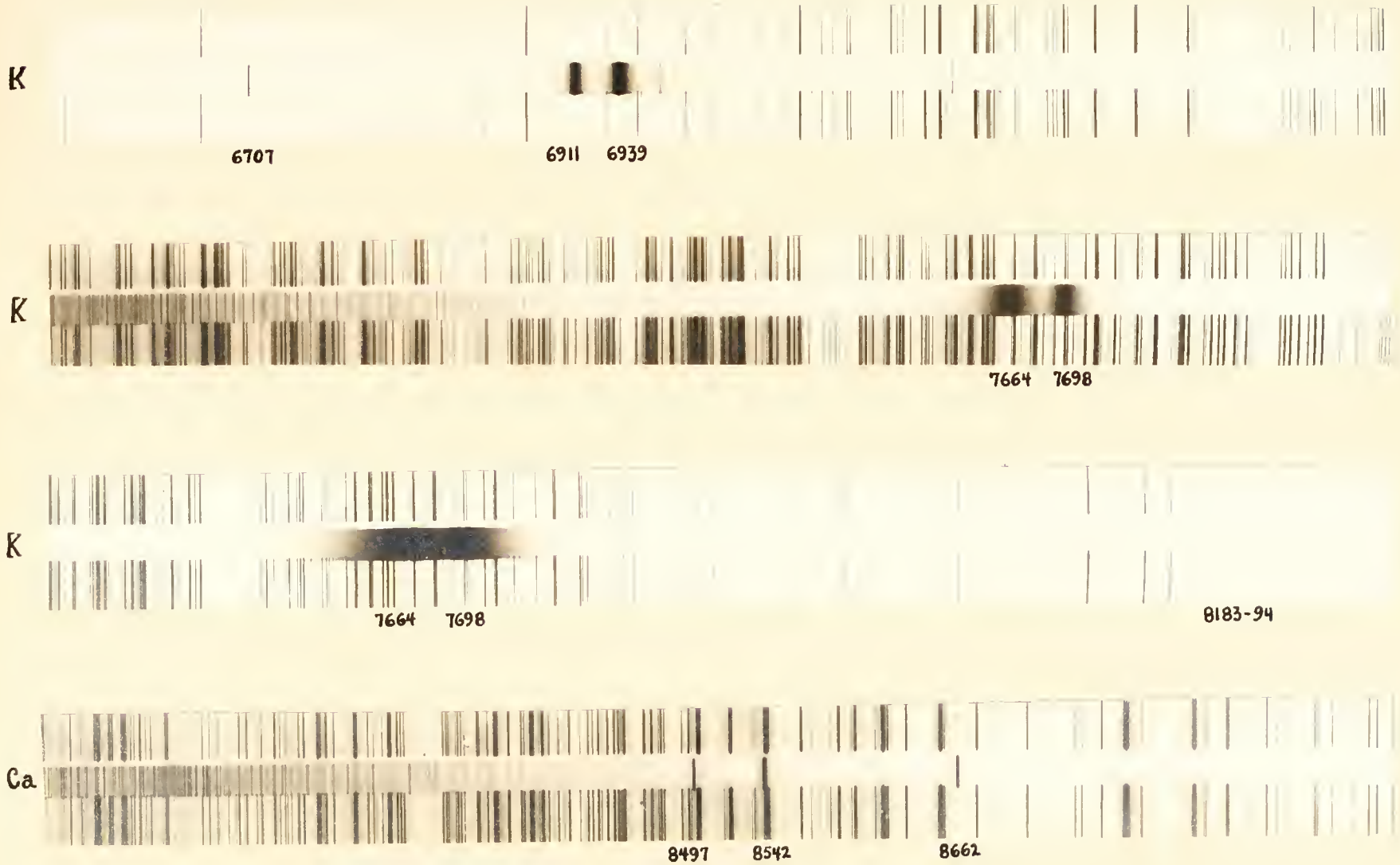
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K
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K
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Ca
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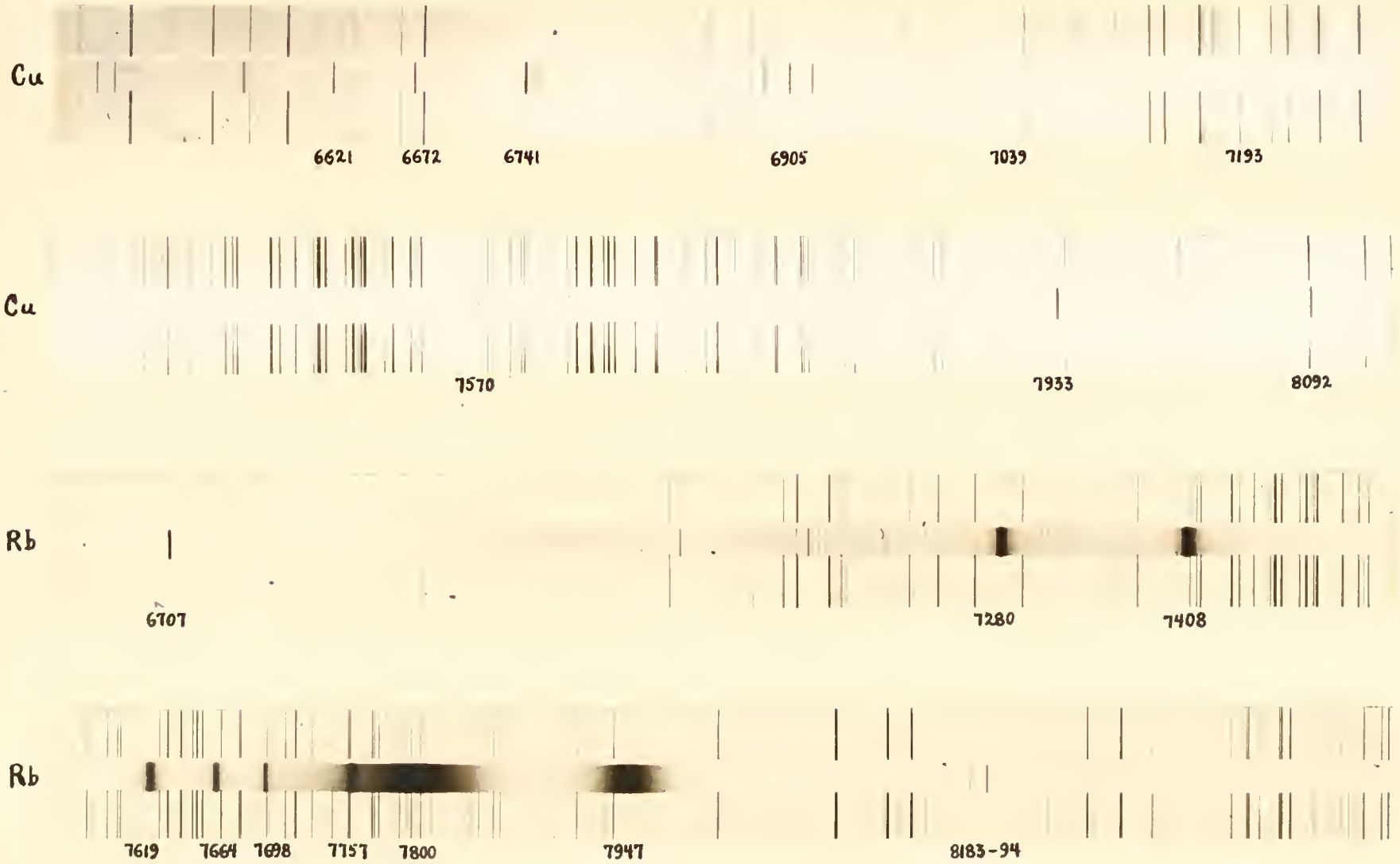
8542
8662

PLATE IV.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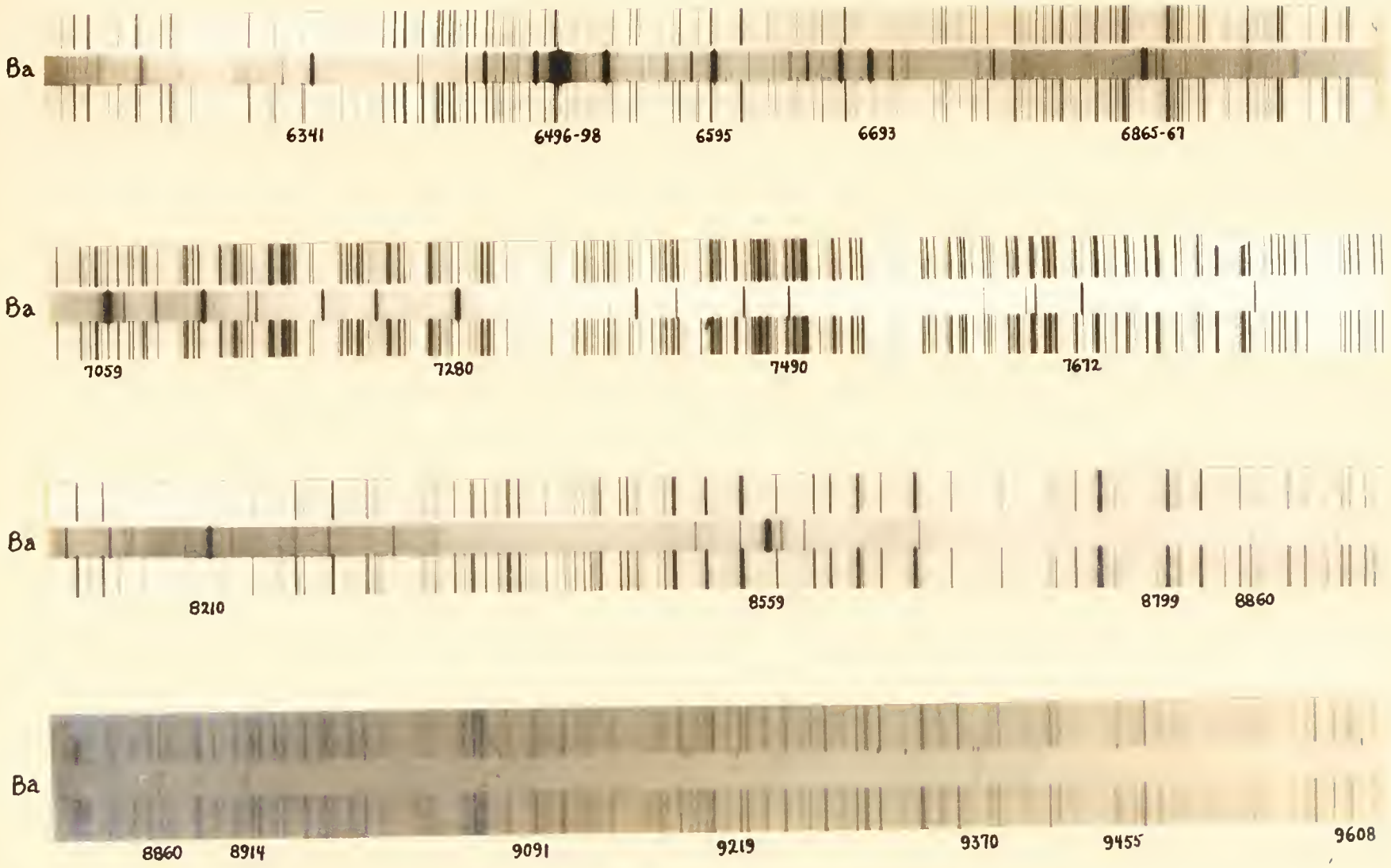
7039
7193
Cu
7570
7933
8092
Rb
6707
7280
7408
Rb
7619
7664
7698
7757
7800
7947
8183-94

PLATE V.


Ba
6341
6496-98
6595
6693
6865-67
Ba
7059
7280
7490
7672
Ba
8210
8559
8799
8860
Ba
8860
8914
9091
9219
9370
9455
9608

Summary.

Accurate measurements of wave-lengths and determinations of the characteristics of the emission lines in the spectra of the elements are of importance in spectroscopic analysis and for the discussion of regularities in spectra. Such information about the long waves has been delayed chiefly by the insensitiveness of ordinary photographic plates to the red and adjacent infra-red spectral regions. More extensive use of photographic dyes is important for these spectral investigations.

Dicyanin is especially valuable and efficient as a photographic sensitizer for the long waves. The simple proceedure of staining ordinary photographic plates in a mixture of Dicyanin, water, alcohol and ammonia renders the plates quite sensitive to wave lengths from 6000A to 9000A. Such plates were used to photograph the arc spectra of twenty of the chemical elements including the alkali metals, the alkaline earths and elements commonly found in iron as impurities.

The photographs were made in the first order spectrum of a concave grating 640 cm. radius, the grating being mounted in parallel light. Exposures were usually limited to thirty minutes and these sufficed to record waves longer than 9000A in many of the spectra. The second order spectrum of the iron arc was photographed on either side of the first order and the long wave-lengths were obtained from

the standards in the iron spectrum. The wave-length measurements are given on the International scale for the arc spectra of the following elements: lithium,sodium, potassium, rubidium, caesium, copper, calcium, strontium, barium, and magnesium. The wave-lengths range from 5600A to 9600A and the probable error is less than .02A for all lines measured more than twice. The broad and unsymmetrical character of some of the lines imposes a limit on the accuracy obtainable in the measurements.

Frequency differences of doublets in the spectra of sodium, potassium, rubidium, caesium and copper are shown by these wave-length determinations to be constant in most cases to one part in 100,000 in the number of waves per centimeter.

Comparison of the spectra made it possible to detect many impurities in the elements used for light sources. Still more extensive spectral investigations are required in the region of long wave-lengths to identify all the lines correctly.

In conclusion I wish to express my thanks to Professor Ames and to Dr. Burns for their interest and encouragement in this work.

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Biographical Note.

William Frederick Meggers, son of John Meggers and Bertha (Bork) Meggers was born in Clintonville, Wisconsin on July 13, 1888. He received his preparatory education in the Clintonville public school, graduating in 1906. In 1907 he entered Ripon College and received the degree of Bachelor of Arts in 1910. He was graduate assistant in the Physics Department of Ripon College during the following school year. During the next school year, 1911-1912, he studied Physics at the University of Wisconsin and served as an assistant in the Physics Department. The degree of Master of Arts was awarded to him by the University of Wisconsin in 1916. For two years, beginning October 1912, he was an instructor in Physics at the Carnegie Institute of Technology. In 1914 he received an appointment as Laboratory Assistant at the Bureau of Standards, and was promoted to Assistant Physicist in 1916. While at the Bureau of Standards he pursued studies in Physics and Astronomy under Dr. J. A. Anderson of the Johns Hopkins University. He entered the Johns Hopkins University in October 1916, taking Physics, Mathematics and Astronomy as his subjects. During the year 1916-1917 he attended lectures given by Professors Ames and Wood in Physics and Professors Cohen and Bateman in Mathematics.